ASSIGNING THE COMPLICATED DISPERSED FLUORESCENCE SPECTRUM OF PhCCCN

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The dispersed fluorescence spectrum from the S_1 origin of PhCCCN is reported. This molecule, which consists of a cyanoacetylene chain fused to an aromatic phenyl ring, is a potential candidate for astronomical detection. The high resolution spectrum was obtained under jet-cooled, gas-phase conditions with a rotational temperature of roughly 2 K, and appears to encode rich information about the vibronic coupling in this species. The experimentally observed peaks are assigned to emissions from the S_1 ($\tilde{A}\,^1B_2$) origin to a_1 vibrational levels of the ground state, which are dipole allowed and governed by FC factors, and to b_2 vibrational levels of the ground state, made possible by vibronic interactions between S_1 and S_2 ($\tilde{B}\,^1A_1$) states. The S_0 vibrational structure features a combined Fermi and Darling-Denison resonance near $950\ \mathrm{cm}^{-1}$, which is accurately reproduced by diagonalization of an effective Hamiltonian containing the three a_1 states involved. A KDC Hamiltonian is employed to treat the vibronic b_2 features.